

# 3D Multiscale Lithium-Ion Cell Modeling for $\text{LiFePO}_4$ Freeze-Casted Electrode Structures Using Synchrotron X-Ray and FIB/SEM Tomography

Robert Franke-Lang,\* André Hilger, Ingo Manke, Sara Zavareh, Maged F. Bekheet, Aleksander Gurlo, and Julia Kowal

The performance of batteries and the associated operating areas depend, among other things, on the 3D microstructures of the electrode materials, and thus fundamental research is required in the field of electrode design. A multiscale microstructure-resolved 3D model is developed that investigates two different  $\text{LiFePO}_4$  freeze-casted electrode structures, that is, cellular and lamellar. The microstructure is simulated directly from the X-ray computed tomography data and the nanostructure is combined with the pseudo-2D simulation approach, where the morphological parameters and the distribution of the binder, carbon, and  $\text{LiFePO}_4$  are obtained from ex situ focused ion beam scanning electron microscopy measurements. The discharge performance shows that the lamellar structure exhibits a lower ohmic overvoltage and achieves a higher gravimetric capacity compared to the cellular structure, even though both electrode materials have the same porosity and amount of active material. The simulation reveals that the performance is not only directly influenced by the lithium-ion transport through the porous structure but also by the current distribution through the active material. Based on these insights, lamellar electrode structures should be considered for next-generation battery electrodes. The modeling approach can assist in electrode fabrication by identifying defects or suggesting better structural parameters.

## 1. Introduction

Many countries have already committed themselves to the objective of not permitting any new registrations for vehicles with combustion engines within a time horizon of 5–10 years. In addition, the demand for renewable energies is becoming greater and greater in order to stop or counteract climate change. However, regarding to the electrification of the powertrain and the use of renewable energies efficiently, innovative and enhanced electrical energy storage solutions are needed. Li-ion batteries are the leading technology, especially in the e-mobility sector, but their energy and power density are relatively low compared to fossil fuels. However, research into new electrolytes,<sup>[1,2]</sup> separators,<sup>[3–5]</sup> anode materials,<sup>[6–8]</sup> and cathode materials still offers potential for optimization.<sup>[9–11]</sup> Lithium iron phosphate ( $\text{LiFePO}_4$ ), also denoted as LFP, is a promising cathode material due to its good price–performance ratio, good cycling stability, high robustness, satisfying cycle life, wide temperature range (–30 to 60 °C) and good rate capability.<sup>[12–15]</sup> Unfortunately, the energy density is relatively low compared to the common cathode materials.<sup>[16]</sup> An enhanced structure of the electrode, which

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allows to utilize the full potential of the electrode, is a possibility to improve the energy density and the rate capability.<sup>[17,18]</sup> Therefore, new production methods are needed that allow better electrode structures for unhindered ion flow. A promising method could be freeze casting.<sup>[19–22]</sup> Freeze casting (ice templating) is a two-step mechanism. The first step is the solidification of the solution or slurry using deep temperatures. The second step is the sublimation, which removes the solvent (in most cases water). With this technique it is possible to manufacture porous materials with different morphologies. These morphologies depend on the crystal growth character of the solvent.<sup>[19]</sup> In recent years, this method has been used primarily in the production of porous ceramics,<sup>[23]</sup> or functional electrodes in fuel cells.<sup>[24]</sup> Especially in ceramic research, freeze casting is often mentioned in combination with a third step, the sintering. Porous electrodes with low tortuosity have generally a more efficient ion flow when discharge rates are increased, and therefore provide a more uniform lithiation.<sup>[25]</sup> The charge and discharge rates can also be enhanced by a porous structure with small particles.<sup>[26]</sup> Thus, this technique is also gaining more and more importance for the optimization of battery electrodes. Nevertheless, the freezing process is an essential factor for reproducible and reliable results.<sup>[20]</sup> The freezing parameters (e.g., temperature and cooling rate) are significant for the morphologies and thus for the porosity. Besides the freezing parameters, it is also possible to manipulate the structure by adding or varying ice-structuring agents (e.g., binders, dispersants, and additives) in the slurry.<sup>[22,27–29]</sup> The pore structure is distinguished into isotropic structure (mostly cellular) and anisotropic structure (e.g., lamellar, dendritic, or honeycomb).<sup>[21]</sup> In preliminary work, we have shown experimentally that the lamellar structure should be favored in order to improve power and energy density.<sup>[18,22]</sup> This is due to the lower tortuosity and the associated better transport kinetics of the lithium ions.<sup>[30]</sup> Besides the low tortuosity, the improved mechanical stress, which leads to better cycle numbers,<sup>[26,31]</sup> and the good electrical as well as the thermal conductivity are often emphasized.<sup>[32]</sup> In addition, the lamellar structure offers improved access to the active materials and increases the active surface whereby higher current rates can be achieved.<sup>[17,33]</sup> In a theoretical consideration, we have already been able to demonstrate how a superior macrostructure has a positive effect on the electrode performance at higher discharge currents.<sup>[18]</sup> For this purpose, a pseudo-2D (P2D) model originated by Doyle, Fuller, and Newman (DFN model)<sup>[34]</sup> was developed and geometrically modified to create a perfect lamellar and cellular structure. However, some unanswered and open questions remain, for example, how inhomogeneities, real tortuosities, and the influence of the real microstructure within the active material will affect the performance. One possibility for obtaining the real electrode structure on macro scale is X-ray computed tomography (X-ray CT).<sup>[35,36]</sup> Tomography (“sectional image”) generally describes a non-invasive optical measurement of 3D distributed quantities. In most cases, the image is obtained from single radiographs with the help of a reconstruction algorithm. Usually, laboratory X-ray tomography<sup>[37–41]</sup> is used, but synchrotron X-ray tomography<sup>[42–44]</sup> and neutron tomography<sup>[45–47]</sup> can also be used depending on the requirements, especially the desired contrast and the spatial resolution. 3D imaging techniques provide a deeper insight into the inner structure of materials and can

reveal complex processes.<sup>[35,48,49]</sup> Furthermore, in combination with additional electrical measurements and modeling, it is possible to obtain a detailed prediction for the performance and lifetime of batteries and components.<sup>[50–53]</sup> However, the microstructure of the electrode is usually not measurable due to the limited spatial resolution of the X-ray CT and the poorly distinguishable attenuation coefficients of the materials. Furthermore, the microstructure is a very complex function of particle size and distribution, binder, and other additives such as carbon, tortuosity, and porosity.<sup>[54–56]</sup> In contrast, with a focused ion beam scanning electron microscopy (FIB/SEM) it is possible to achieve a very high spatial resolution at the nanoscale,<sup>[57,58]</sup> which allows a good separability of the different materials within the microstructure. However, the disadvantages are the destructive character of the method and the comparatively small sample volume. The combination of both methods is becoming more and more standard in the investigation of lithium-based batteries.<sup>[59–63]</sup>

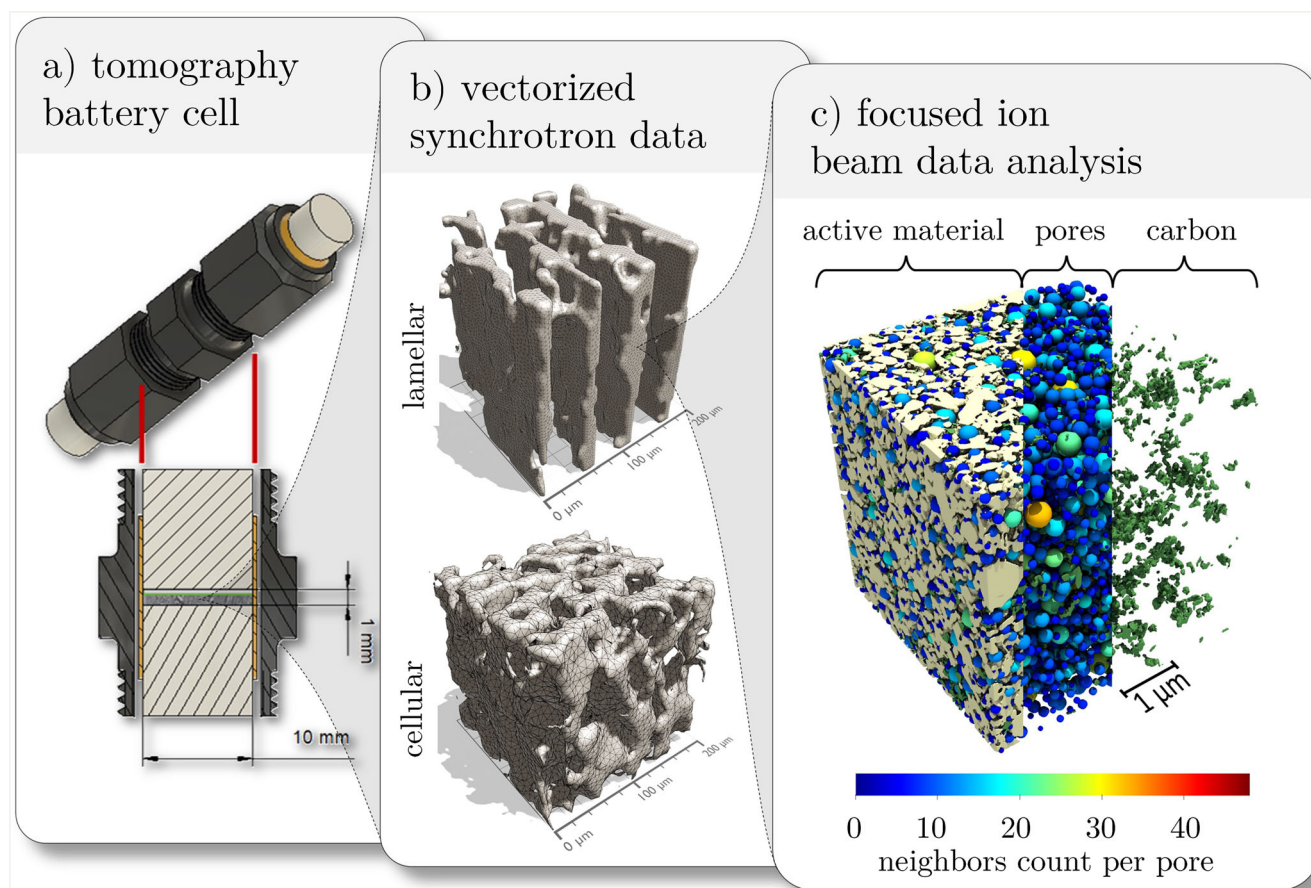
The present work is intended to increase the understanding of LFP cell properties under real electrode structures in order to enhance both the porous electrode design and the cell performance of lithium-ion batteries. Therefore, the already implemented P2D approach was extended to real 3D measured electrode microstructures.<sup>[18]</sup> The complex electrode structures were determined by a combination of synchrotron X-ray tomography and FIB/SEM investigations in order to obtain the multiscale parameters of the cathode material. The commercial software COMSOL Multiphysics was used for the numerical solution to get more insights of the performance during operation. For the validation of the model and the comparison of the previous 2D assumptions, two targeted structural cathodes, that is, cellular and lamellar, were manufactured with the help of the unidirectional freeze-casting method. The electrodes were assembled in half cells and electrically characterized by discharge tests at different current rates.

## 2. Results and Discussion

### 2.1. 3D Characterization of Microstructural Parameters

#### 2.1.1. Measurement Setup and Acquisition

A lithium-ion cell has different length scales depending on the component and the materials used, which complicates both the use of an appropriate spatially resolved structural measurement method and the physicochemical simulation. **Figure 1a** illustrates the assembled cell (Swagelok) down to the dissection of the electrode at the microstructural scale, which is often only a fraction of the measuring cell. The disc-shaped components (e.g., anode, separator soaked in electrolyte, and cathode) are stacked in the center of the cell and are pressed together by the current collectors, which are electrically isolated from each other (**Figure 1a**). Synchrotron-based tomography (s $\mu$ CT) with a resolution of  $\approx 1.2\ \mu\text{m}$  was used for a non-destructive investigation of the cathode material (**Figure 1b**). The coarse structure of the two samples under study here were determined using s $\mu$ CT resulting in a vectorized 3D model for both the cellular and the lamellar samples. In addition to the 3D data, the physical quantities tortuosity and porosity of the coarse structure were determined. Since the fine structure parameters are in the nanometer range



**Figure 1.** Exemplary schematic representation of the applied 3D tomographies. a) The assembled cell (Swagelok) and its cross-section. b) Small and vectorized portions of the electrode materials that have been imaged by means of synchrotron radiation. c) The dataset acquired with FIB/SEM tomography. The visualized volume shows the extracted active material, the largest spheres that can be fitted into the pore network and the extracted carbon particles inside the pore system. The fitted spheres are colorized depending on the number of their connected neighbors.

and carbon and pores have a similarly low X-ray attenuation coefficient, the knowledge about the real microstructure usually remains hidden. In order to overcome this circumstance, post-mortem FIB/SEM measurements with a voxel size of 10 nm have been conducted. A resulting 3D volume reconstruction and a part of the conducted analysis is visualized (Figure 1c). The combined use of the  $\mu$ CT and the FIB/SEM imaging techniques allows the detection of both the nanoscale and microscale morphology.

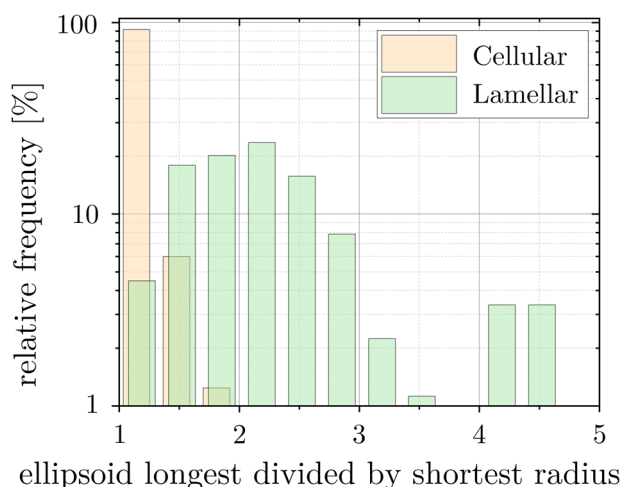
A detailed description of the measuring protocol and data post processing is given in Section 4.

### 2.1.2. Volume Data Analysis

On the micrometer scale (see Figure 1b), the lamellar sample has a porosity of 55.2%, while the cellular sample was slightly denser with a porosity of 53.0%, but these porosities are not generally true, as will be discussed later in this section. However, the main difference is not in porosity but in morphology. While the cellular sample is isotopically structured, the lamellar sample is laminar and thus strongly non-isotropic. The difference is particularly evident when ellipsoids are fitted to the material structure and the fitted inner radii are compared (especially the

quotient of the longest and shortest ellipsoid radius). This can be done by first segmenting the structures into their morphological substructures using a watershed transformation. After segmentation, the former complex morphology consists of morphologically much simpler and smaller grains like particles (cellular) or plates (lamellar), which can be individually fitted with ellipsoids. The resulting ellipsoid distributions are shown in Figure 2. With an average quotient of  $1.12 \pm 0.03$ , the cellular sample shows a spherical substructure, while the lamellar substructures are much more elongated with an average quotient of  $2.23 \pm 0.5$ .

To analyze the material in more detail, the underlying nanostructure of the samples is discussed next. At this scale, the previously described differences are no longer detectable because the FIB/SEM region of interest is 150 times smaller than the synchrotron region. However, it is the tortuosity and the real material densities and distributions that are of interest here, since the porosities shown previously do not represent the actual values due to resolution limitations. For this purpose, the classified FIB/SEM data were filtered with the watershed algorithm as shown before. This time, however, the pore space was also segmented to allow the construction of a virtual pore network. The main resulting distributions are shown in Figure 1c. The high-resolution FIB/SEM tomography shows for the lamellar sample



**Figure 2.** Comparison of the structural difference of the cellular and the lamellar sample based on synchrotron imaging. While the substructures of the cellular sample show a sphere-like behavior the lamellar structure is more elongated.

that the areas previously classified as bulk are actually 51.8% open pores, 46.4% active material, and 1.8% carbon (shown in Figure 1c). The measurement for the cellular sample shows a material composition of 45.9% active material and 1.8% carbon. Therefore, the total porosity for the lamellar sample is 78.4% while the cellular sample is 77.6%. The LFP density is determined to be  $0.75 \text{ g cm}^{-3}$  for the lamellar sample and  $0.78 \text{ g cm}^{-3}$  for the cellular sample. Compared to the carbon-based additives, the weight percentage of active material in both materials is  $\approx 97.6\%$ . Due to this low amount of carbon-based additives, neither a pure carbon conducting network nor an interconnected network was detected.

**Figure 3a** shows the sub-particle size distribution of the active material, which is a typical lognormal distribution with a mean spherical equivalent radius of  $0.12 \pm 0.04 \mu\text{m}$ . As shown in the 3D rendering of the reconstructed FIB/SEM measurement, these active particles form an open porous matrix containing additional carbon material. The pore network was virtually filled, as shown by the porosimetry measurement in Figure 3b. The network has a bottleneck in the diameter range of about 30 to 83 nm, that is, virtual spheres of size 30 nm can penetrate 90% of the pore network, while spheres of size 83 nm can penetrate only 10%. The network is well interconnected, so that each pore is connected to an average of  $8.5 \pm 5.2$  pores, as shown in Figure 3c. With the precise structural information on the nanometer scale, it is finally possible to calculate the simulation-relevant geodesic tortuosity through the material itself. The tortuosity for the material is 1.04, while through the pore system it is 1.03.

## 2.2. Simulation of the Measured Microstructures

For an understanding of the relationship between the real microstructures and the experimental behavior of the battery, the reconstructed 3D cathodes were simulated at different discharge current rates. The anode was implemented as an ideal metallic lithium electrode and formed the upper boundary condition of

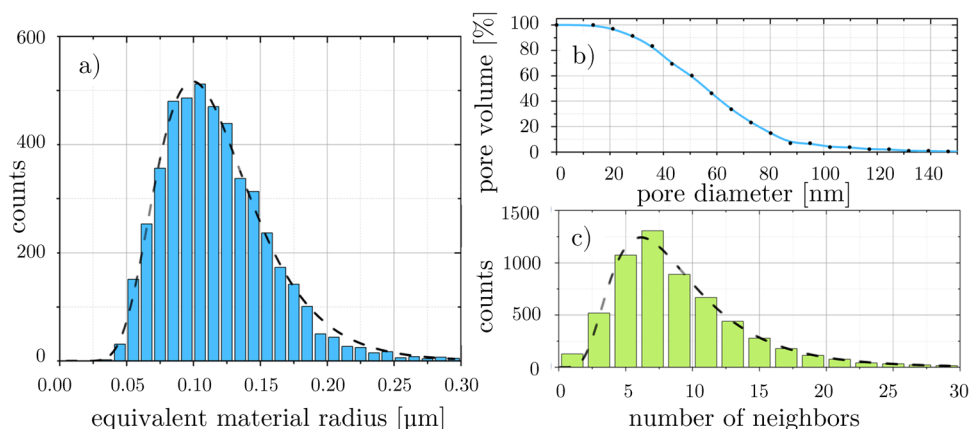
the porous polyethylene separator. The cathode was confined by both the separator above and the solid aluminum current collector below. The pore volumes were soaked with lithium hexafluorophosphate ( $\text{LiPF}_6$ ) electrolyte in a mixture of propylene carbonate, ethylene carbonate, and dimethyl carbonate (PC/EC/DMC, 10:27:63 by volume). The material, simulation and geometry parameters are provided in Section 4.

### 2.2.1. State of Lithiation

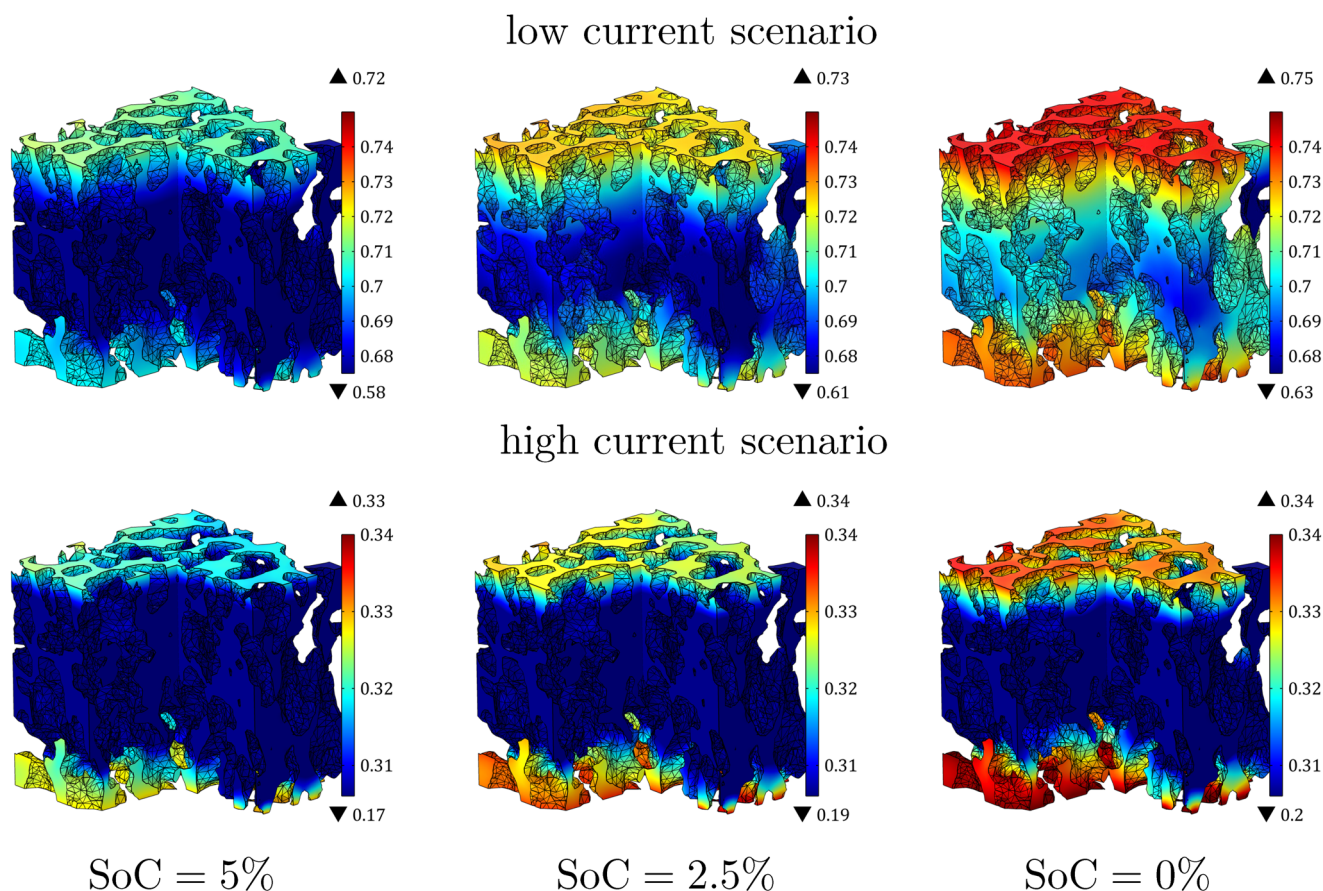
The state of lithiation (SoL) is defined by the ratio of the average lithium-ion particle concentration to the maximum possible lithium-ion particle concentration. It represents a measure of the utilization of the electrode under different conditions. **Figure 4** shows the SoL of the cellular LFP electrode at two different discharge currents (0.5C—low current scenario, 2C—high current scenario) and three different state of charges (SoCs, 5%, 2.5%, and 0%) near the end of the discharge process. The SoC is related to the constant current discharge capacity from 3.6 to 2.5 V. The upper limit of the color scaling was set to the maximum lithiation at 0% SoC and the lower limit was set to 90% of the upper limit for each current rate, respectively. The results illustrate that at low current rates the cathode is more lithiated at the top. In the last five SoC steps a slight gradient is developed from the boundary layers to the inner cathode material. The lithiation homogeneity index (LHI), which describes the degree of uniformity or homogeneity related to the lithiation state of the electrode, is introduced as the quotient of the minimum SoL and the maximum SoL. A value of 100% indicates a perfectly uniform lithiated electrode where each part of the electrode has reached maximum lithiation. For the low current scenario, the LHI with respect to the maximum SoL of 0.75 and the minimum of 0.63 is 84% at 0% SoC. In comparison, at high current rates, the gradient is amplified, and the related LHI is only 58.8%. A strong depletion zone is formed at the center of the cathode. This effect can be explained by the different time constants between electrode reaction and mass transfer. High current rates require a high concentration of free lithium ions in the electrolyte. If the ion flux is reduced due to low diffusion coefficients, a low porosity, a high tortuosity, or low temperatures, the entire thickness of the electrode can no longer be sufficiently supplied with lithium ions, which results in an increasing gradient. Consequently, the full utilization takes place primarily near the separator and the current collector, which significantly increases the inhomogeneity of the lithiation along the path of the ion flux. Furthermore, complete lithiation of the cathode material depends, among other things, on the particle size and a sufficient solid-state diffusion. These quantities become more important at higher current rates. The outer regions of the particles are almost completely lithiated and cannot absorb any further lithium ions, but the core remains unlithiated, if the particles are very large and the solid-state diffusion is very slow in comparison to the current rate,<sup>[64]</sup> thus reducing the average lithium-ion particle concentration of the LFP electrode and the discharge capacity accordingly.

The SoL of the lamellar structure at the same conditions and the same color scale format as for the cellular LFP electrode is shown in **Figure 5**. It can be seen that the LHI for each current rate improves slightly to 86.7% for the low current scenario and





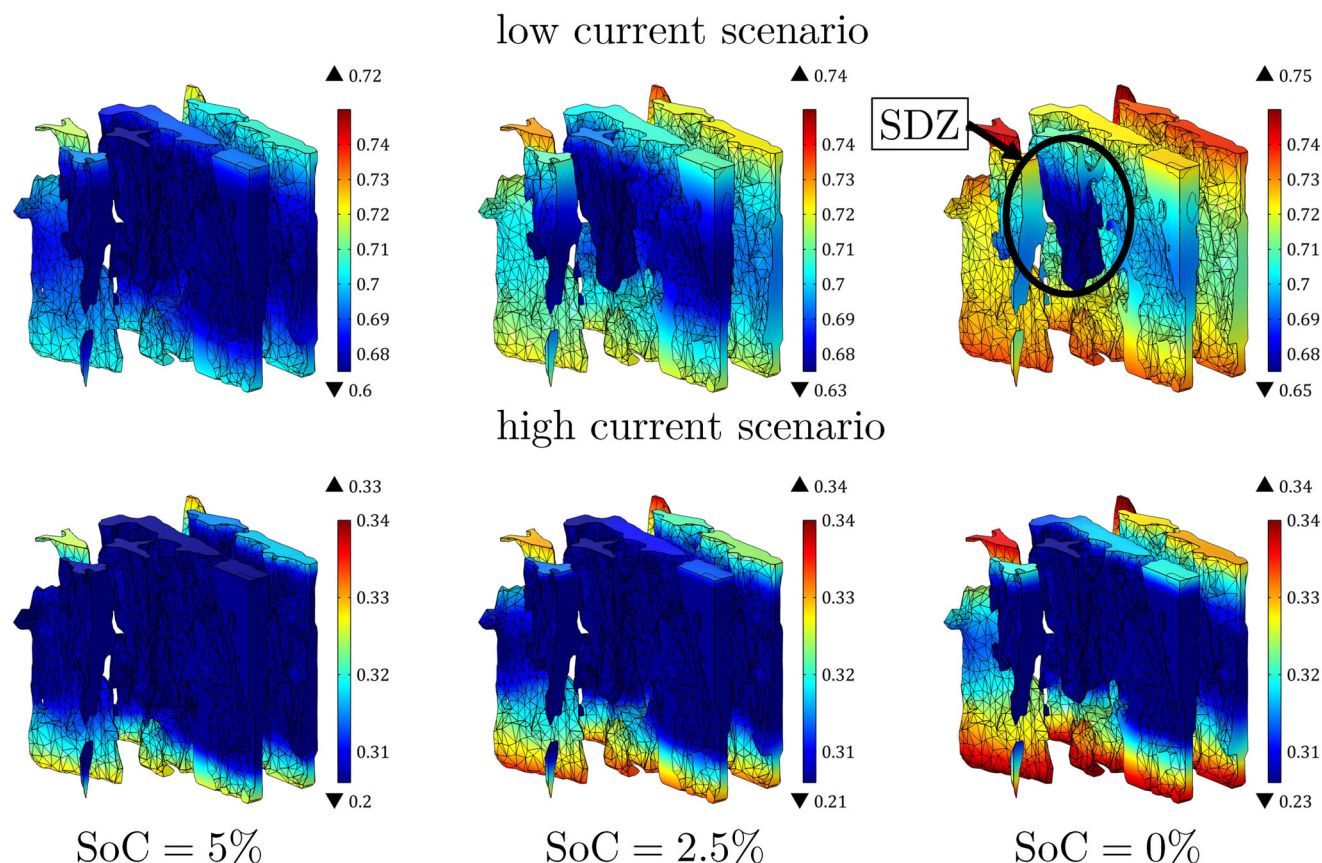
**Figure 3.** Structural data of the nanometer scale. a) The distribution of the active primary particles the whole electrodes are built of. b) The result of a virtual porosimetry measurement. c) The number of connected neighbors of each pore inside the porous nanostructure. In addition, both distributions (a) and (c) are fitted with a logarithmic Gaussian function.



**Figure 4.** Evolution of the SoL based on the average lithium-ion particle concentration within the cellular microstructure at low current and high current during the end of discharge (SoC ≤ 5%). The cut-out allows a view inside the electrode domain. The top region is adjacent to the separator and the bottom region to the current collector.

to 67.6% for the high current scenario. However, the characteristic of the lithiation remains the same. Also, the limited lithiation of the particles at higher current rates cannot be improved by changing the morphology of the electrode, since the limiting factors are the solid-state diffusion and the particle size, both

of which are unchanged in the simulation and experiment. As we have already shown, this statement is only applicable as long as there are valid and sufficiently large transport paths for the electrolyte within the entire electrode structure, which is the case here for both the cellular and the lamellar structure.<sup>[18]</sup> If



**Figure 5.** Evolution of the SoL based on the average lithium-ion particle concentration within the lamellar microstructure at low current and high current during the end of discharge ( $\text{SoC} \leq 5\%$ ). The cut-out allows a view inside the electrode domain, which reveals an SDZ. The top region is adjacent to the separator and the bottom region to the current collector.

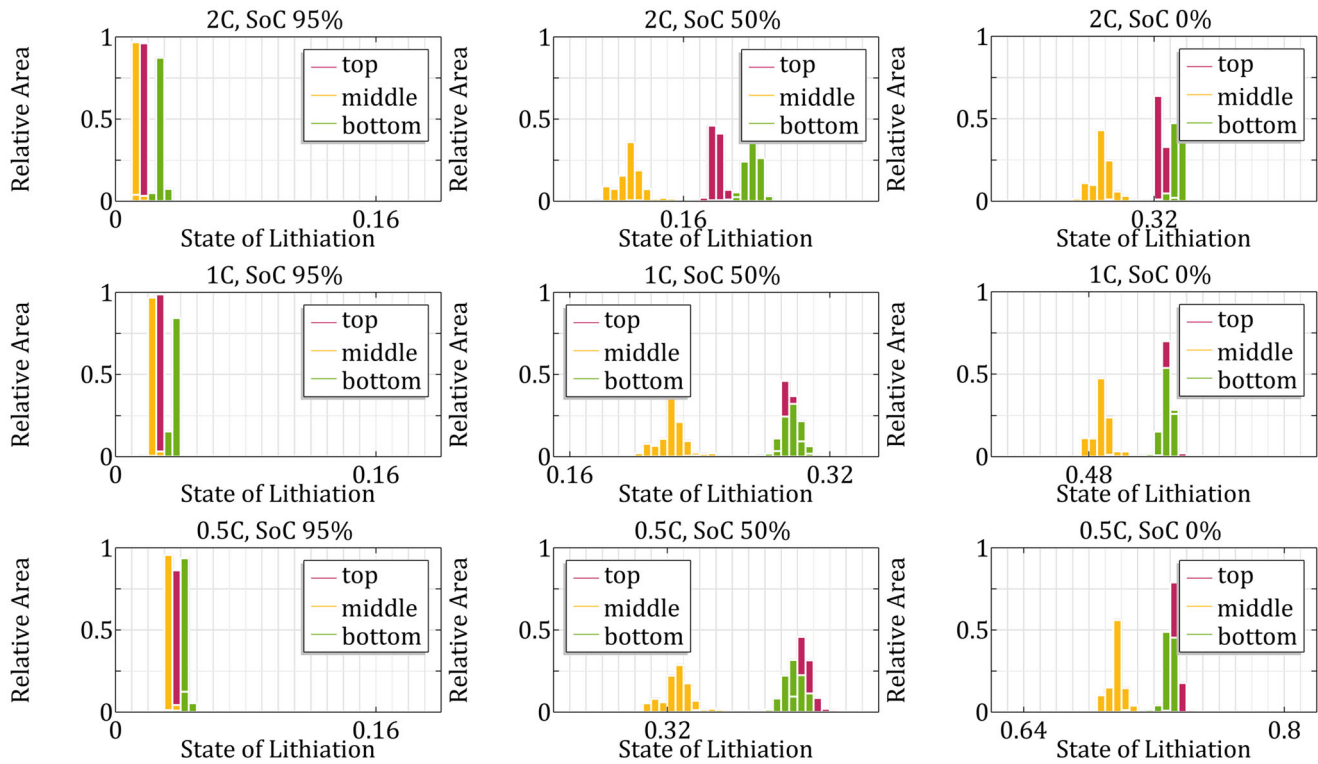
these conditions are not met, mass transport through the active material dominates, which leads directly to an increase in the solid-state diffusion length. In Figure 5, a semi-material dead zone (SDZ) can be seen at the center of the sample due to a coincidence. Unlike a full-material dead zone (FDZ), where the material has no electrical contact with the current collector, the SDZ is still connected to the electrically conductive main material at a small point. Depending on the ratio of contact area to material, SDZs can significantly decrease the capacity due to the reduced current conductivity at the bond points. Figure 5 indicates for the low current scenario that only in the SDZ the lithiation state ranges from 0.65 to 0.7, which corresponds to 6.6% less lithium insertion compared to the maximum SoL of 0.75 at 0% SoC. Without the SDZ the LHI of the lamellar structure is increased to 93.3%.

Figure 6 (cellular) and Figure 7 (lamellar) show the SoL as a function of the initial, intermediate, and final SoC and relative to the area of the cathode in the lowermost ( $5 \mu\text{m}$ ) area near the current collector, the intermediate ( $100 \mu\text{m}$ ) area and the uppermost ( $195 \mu\text{m}$ ) area near the separator, respectively. The 95% SoC was selected since the lithiation state at 100% SoC is zero for the cathode material. In addition, both samples still show a very similar and uniform lithiation at 95% SoC. The quantitative analysis illustrates that the cellular structure has a very dense normal distribution in each region, whereas for the lamellar structure only

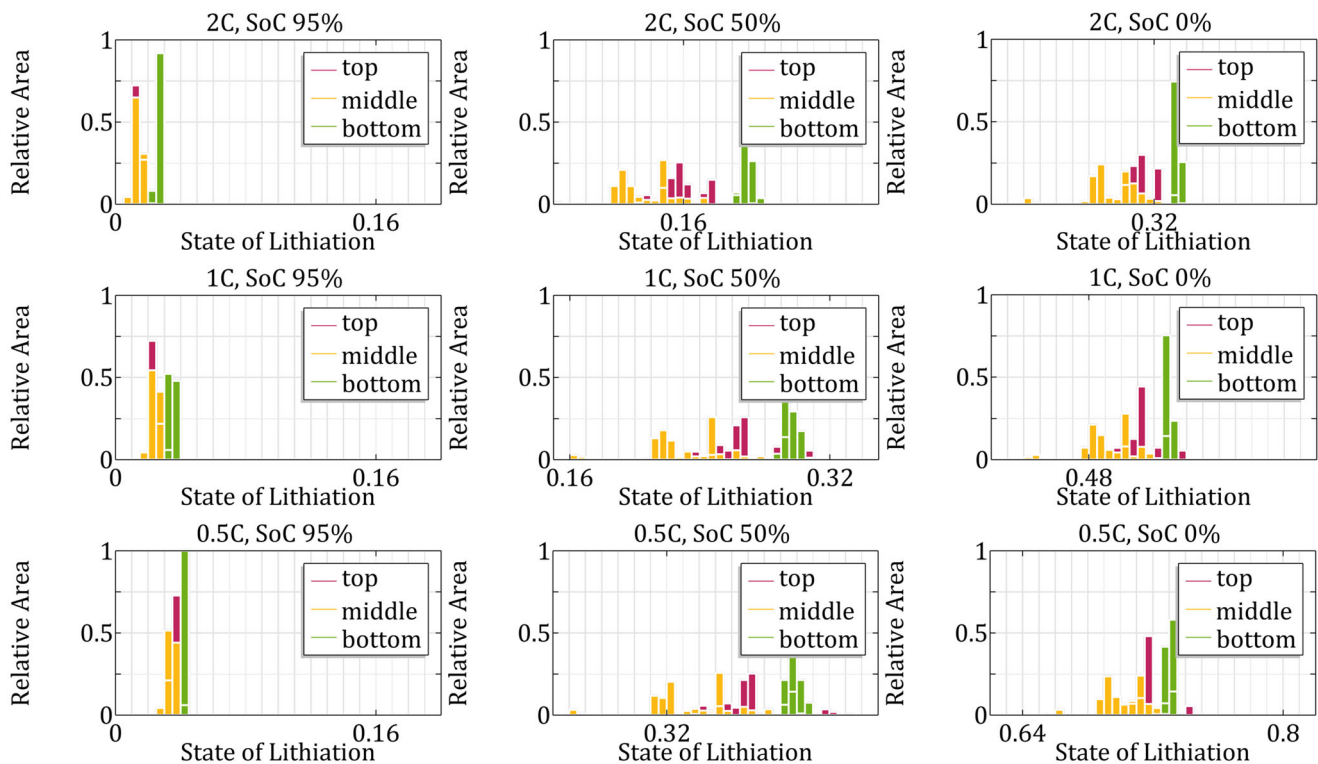
the lower bottom region can be approximately described by a normal distribution. The other regions of the lamellar structure exhibit rather broad distributions, implying that lithiation can vary depending on the lamella structure. Therefore, the cellular electrode through its branching structure and continuous junctions has a more uniform distribution in every cross-sectional area. Nevertheless, the spread between the lower/upper and middle region in the lamellar electrode is much smaller than in the cellular structure, indicating a better homogeneity of the lamellar electrode over the height. In general, as already demonstrated in the qualitative analysis, the upper and lower regions can be lithiated more effectively than the middle region in both samples. This effect occurs relatively independently of the current rate already at 50% SoC.

### 2.2.2. Heat Generation

The heat generation is a decisive factor for both the performance and the degradation of electrochemical cells. In general, higher temperatures benefit charge transport and facilitate both desired and undesired chemical reactions. However, the electrical conductivity of, for example, metals, decreases with increasing temperature. In addition, excessively high temperatures pose an enormous safety risk caused by an accelerated aging and a

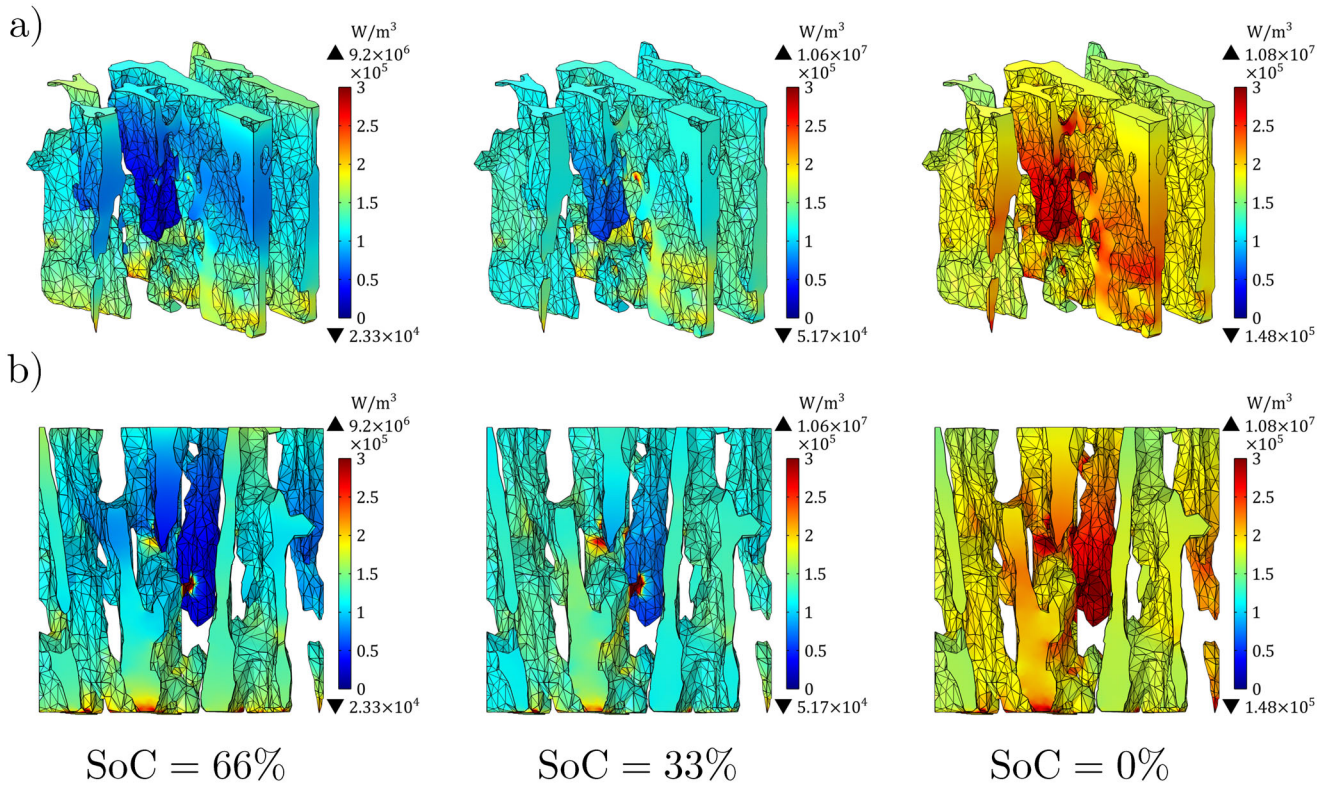


**Figure 6.** Histograms of the SoL of the cellular structure related to three different relative cross-sectional areas (top, middle, and bottom) of the electrode at 0.5C, 1C, and 2C discharge and different SoCs.



**Figure 7.** Histograms of the SoL of the lamellar structure related to three different relative cross-sectional areas (top, middle, and bottom) of the electrode at 0.5C, 1C, and 2C discharge and different SoCs.





**Figure 8.** Distribution of the total heat generation ( $\text{W m}^{-3}$ ) stepwise over the SoC of the lamellar structure at 2C discharge rate. a) The electrode in dimetric view and b) in elevation view, where the heat spot is localized.

possible decomposition of the liquid electrolyte which is used in most of the commercial LIBs.

The volumetric heat generation of the cathode material is affected by a summation of various heat sources. When the external contributions are neglected, the heat generation is mainly determined by the electrochemical processes and the applied charge or discharge currents, which in turn governs the operating temperature of the battery. These heat processes within the domain ( $Q_{\text{dom}}$ ) can be further divided into irreversible heat ( $Q_{\text{irrev}}$ ), reversible heat ( $Q_{\text{rev}}$ ), and heat of mixing ( $Q_{\text{mix}}$ ).<sup>[65]</sup>

$$Q_{\text{dom}} = Q_{\text{rev}} + Q_{\text{irrev}} + Q_{\text{mix}}, \text{ with } Q_{\text{irrev}} = Q_{\text{ohm}} + Q_{\text{ctr}} \quad (1)$$

The reversible process can be caused by an entropy change in the electrode reaction, for example, material phase change.<sup>[66]</sup> The irreversible process can be further decomposed into ohmic heating ( $Q_{\text{ohm}}$ ) and heating due to activation overpotentials ( $Q_{\text{ctr}}$ ). The ohmic heat generation is due to the electrical and ionic charge transport in the solid conductor material and the electrolyte.

$$Q_{\text{ohm}} = - (i_s \cdot \nabla \phi_s + i_l \cdot \nabla \phi_l) \quad (2)$$

where,  $i_s$  is the electric current and  $\phi_s$  is the electrode potential of the solid conductor material and  $i_l$ ,  $\phi_l$  of the liquid phase, respectively.

The heat of mixing is associated with a local concentration gradient from the bulk to the surface; since the gradient is very small, the term is negligible.

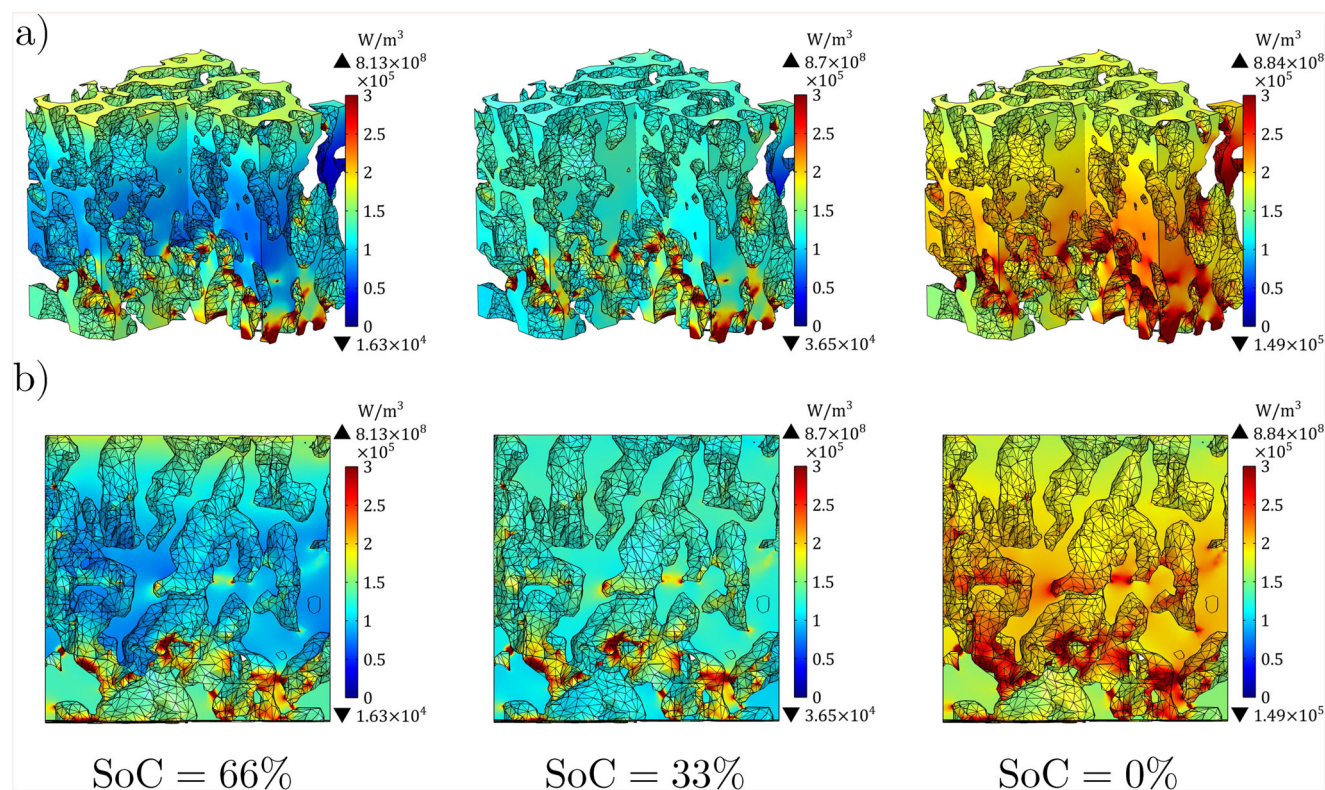
$$Q_{\text{mix}} \approx 0 \quad (3)$$

The activation overpotential takes place at the surface of a particle  $a_k$  in the porous electrode. The local charge transfer from the electrolyte to the particle with the local current density  $j_k$  can be thought of as a finite reaction rate, resulting in the activation overpotential  $\eta_k$ .

$$Q_{\text{ctr}} = \sum_k a_k j_k \eta_k \quad (4)$$

**Figure 8** shows the total heat generation stepwise at 66%, 33%, and 0% SoC of the electrode domain for the lamellar structure at 2C discharge rate. The color scale was limited to  $300 \text{ kW m}^{-3}$  for all graphs. In **Figure 8**, a local heat spot is formed at the junction near the SDZ that is not directly contacted to the current collector. This can be attributed to the ohmic component since the electron current is locally increased by the cross-sectional constriction. This hotspot also heats the adjacent material over time, resulting in an inhomogeneous heat distribution within the electrode structure. In the cellular electrode (see **Figure 9**), more of these junctions are present, resulting in an accumulation of local heat spots and a stronger heating electrode. The overall heating is also favored by the higher compactness of the active material.





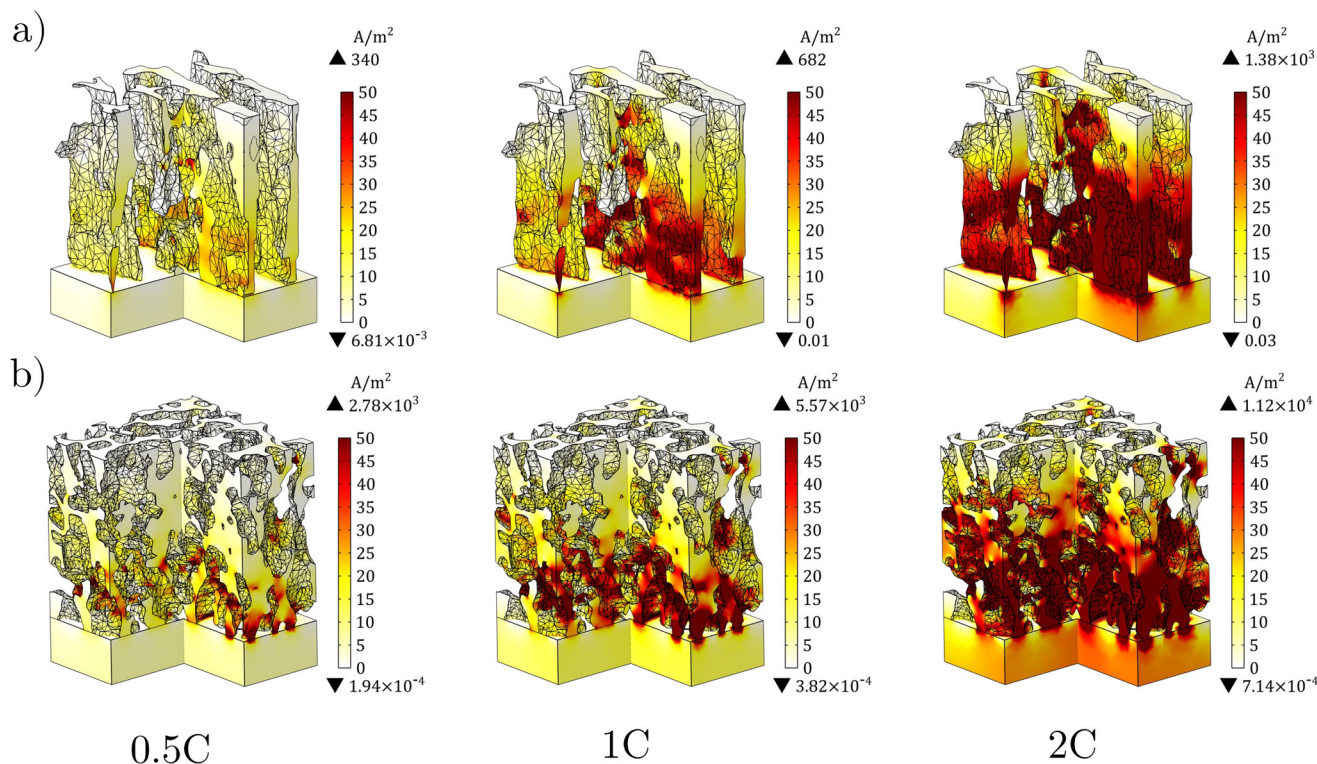
**Figure 9.** Distribution of the total heat generation ( $\text{W m}^{-3}$ ) stepwise over the SoC of the cellular structure at 2C discharge rate. a) The electrode in dimetric view and b) in elevation view.

This effect becomes particularly visible when looking at the absolute value of the local current density vector  $|\vec{j}|$ , illustrated in **Figure 10**. Already at 0.5C, the branching of the cellular structure (Figure 10b) leads to significant local increases of the current density in the lower regions of the electrode near the current collector. At 2C, the entire lower region of the cellular structure is significantly more stressed than the lamellar structure, which is stressed differently from lamella to the lamella.

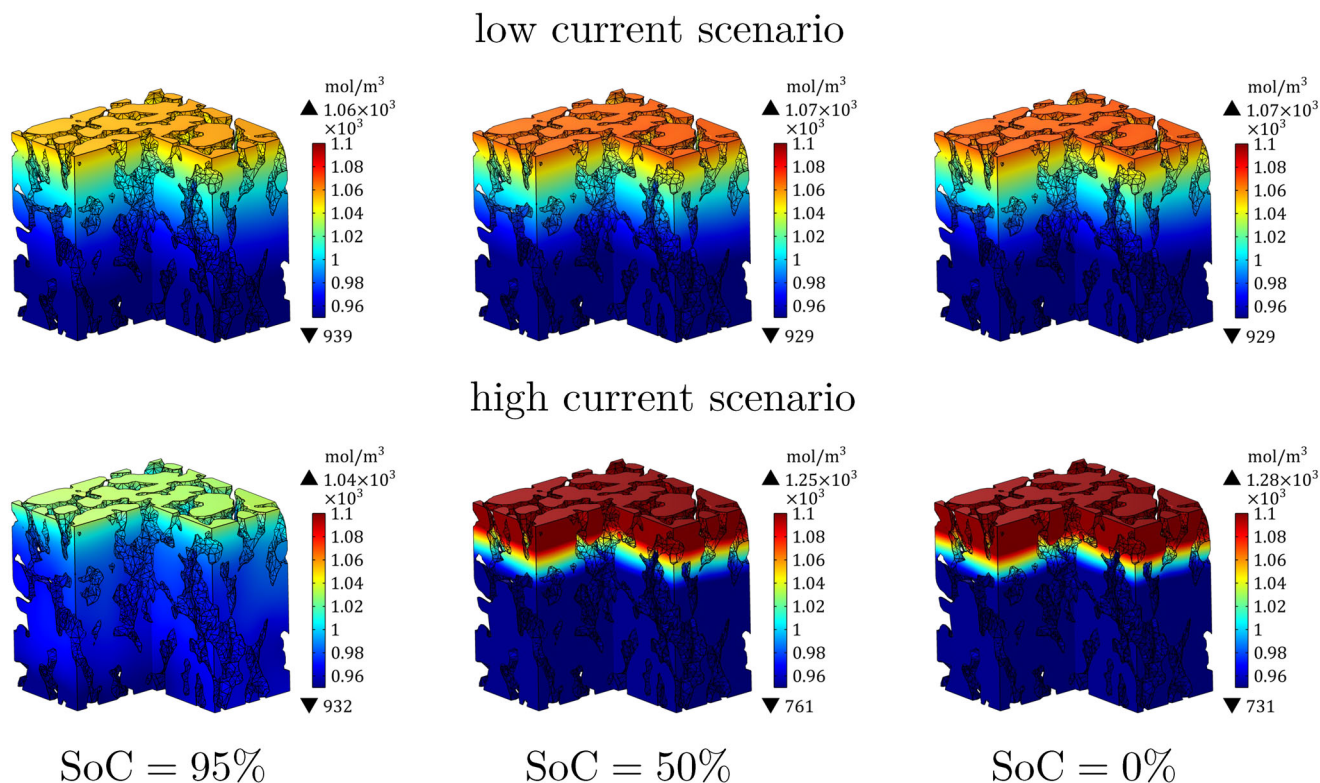
### 2.2.3. Lithium-Ion Concentration of the Electrolyte

The electrolyte plays an essential role within electrochemical cells. Besides being responsible for ionic charge transport and the associated cell performance as well as aging, it is also becoming the focus of ongoing research with regard to safety.<sup>[67,68]</sup> The electrolyte's ability to transport and distribute lithium ions has an influence on the achievable operating energy and the usable power. Key parameters here are the diffusion coefficient, the ionic conductivity, and the pore network.<sup>[18]</sup> Since the same electrolyte was used under the same external conditions in both the lamellar and the cellular experiments, any change in the Li-ion concentration of the electrolyte can be attributed entirely to the electrode structure. The Li-ion concentration of the electrolyte is shown for the cellular structure in **Figure 11** and for the lamellar structure in **Figure 12**, respectively. Here, the change in concentration over the LFP electrode pore volume was mapped at 95%, 50%, and

0% SoC and the low and high current rate under investigation. The color scale was adjusted to  $1100 \text{ mol m}^{-3}$  as maximum and  $950 \text{ mol m}^{-3}$  as minimum. In both Figures 11 and 12, a concentration gradient is observed from the separator to the current collector. This gradient is formed immediately after the discharge current is applied, which leads to a lithium depletion in the lower zone and to an oversaturation in the upper zone. Higher current rates intensify this effect and lead to a sharper separable transition region between the two zones. The maximum gradient is already reached at an SoC of 50% for the low current scenario. For the high current scenario, the maximum slightly increases. The minimum value of the depletion zone continues to decrease over the entire discharge duration for both scenarios and structures. However, after 50% SoC, the decrease of the minimum value is only marginal. The location of the transition region is very identical for both structures with a distance of  $\approx 50 \mu\text{m}$  to the separator. However, the height of the transition region is broadened in the lamellar structure, resulting in a visible wider and softer transition between the depletion and the supersaturation zone. Since the activity, conductivity, and diffusivity are all dependent on the electrolyte salt concentration,<sup>[69]</sup> the ion transport is much more inhomogeneous in the cellular structure than in the lamellar structure, especially at increasing current rates. Also, the minimum value of the Li-ion depletion zone at high current rates within the cellular structure of  $731 \text{ mol m}^{-3}$  compared to the lamellar value of  $822 \text{ mol m}^{-3}$  reveals the hindered ion transport through the cellular structure.

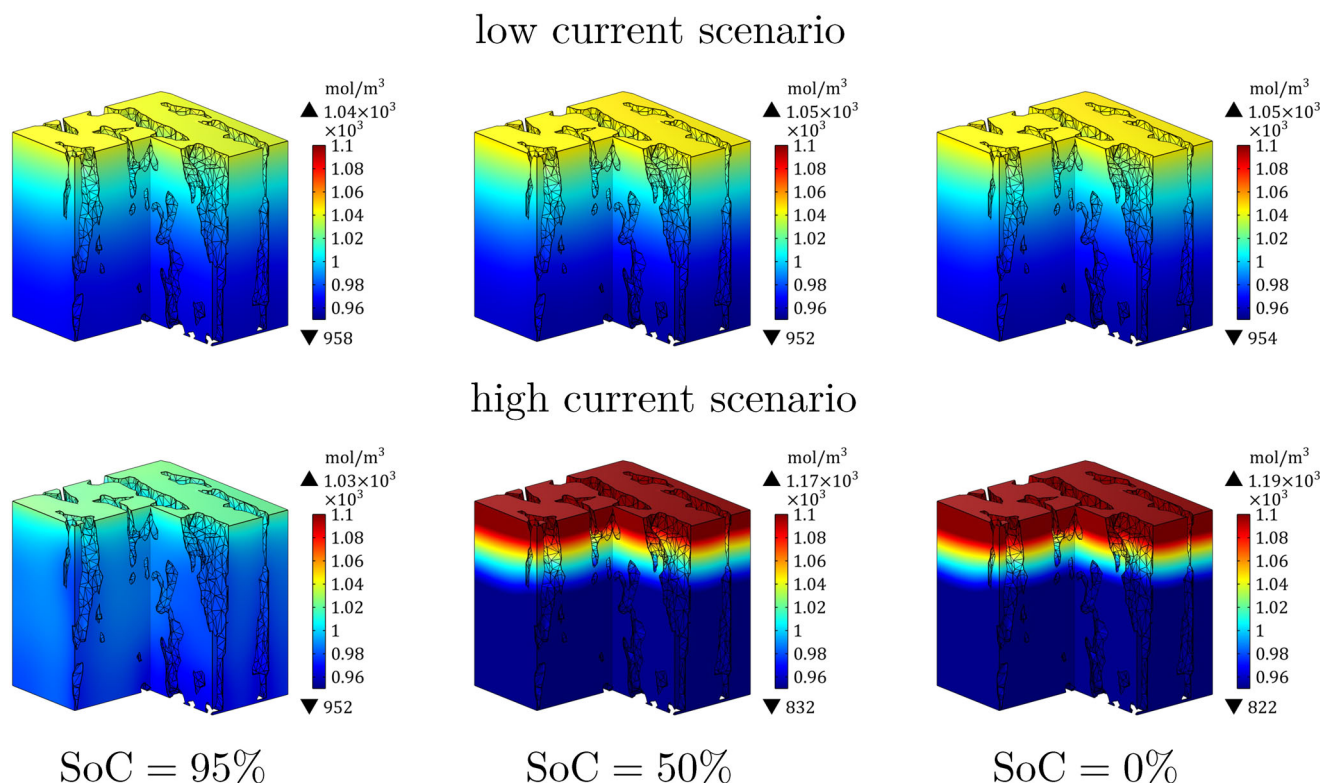


**Figure 10.** Distribution of the current density  $|j|$  (A m<sup>-2</sup>) of the reconstructed cathode and the current collector during discharge at 0.5C, 1C, and 2C, where a) represents the lamellar structure and b) shows the cellular structure.

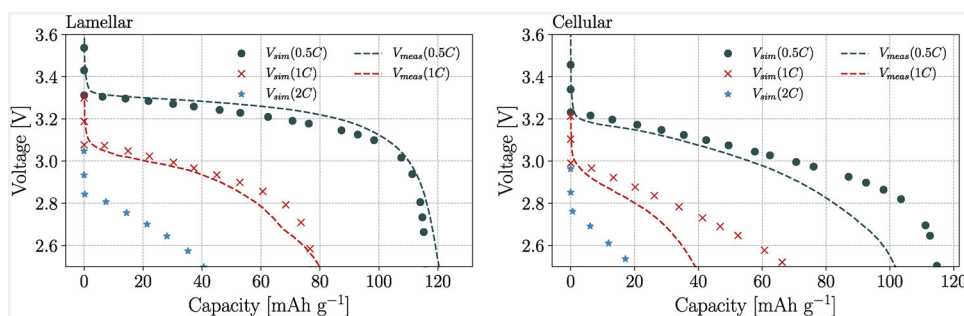


**Figure 11.** Distribution of the electrolyte lithium concentration (mol m<sup>-3</sup>) within the cellular electrode microstructure during discharge at low and high current scenario for different SoCs. During discharge the lithium ions flow from the top (separator) to the bottom (current collector).





**Figure 12.** Distribution of the electrolyte lithium concentration ( $\text{mol m}^{-3}$ ) within the lamellar electrode microstructure during discharge at low and high current scenarios for different SoCs. During discharge the lithium ions flow from the top (separator) to the bottom (current collector).



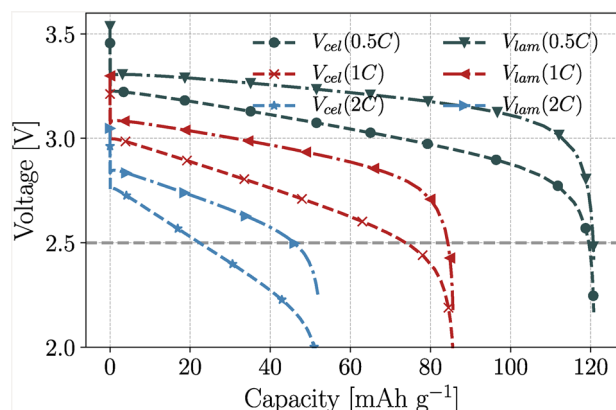
**Figure 13.** Comparison of the discharge behavior related to the achievable gravimetric capacity between experimental measured lamellar and cellular LFP half cells (dotted lines) and the simulated results (marker) at different C rates.

#### 2.2.4. Discharge Behavior

The discharge behavior can provide information about the effective energy and the performance of the electrochemical cell under investigation, depending on the external circumstances. **Figure 13** shows the discharge profiles related to the gravimetric capacity of the half-cell measurements and the numerical simulations at different C rates. In **Figure 13**, the simulation results of the clipped electrode region of the lamellar structure and of the cellular structure were, respectively, compared with the experimental data of the entire half-cell experiments at 0.5C and 1C. In

addition, the high current scenario with a discharge rate of 2C is also shown. Although only an arbitrary  $200 \mu\text{m} \times 200 \mu\text{m} \times 200 \mu\text{m}$  slice of the tomographed electrode structures was used, the simulation results for the lamellar structure were in a good agreement. The numerical simulations for the cellular structure approximated the initial voltage drop well but showed higher deviations in both voltage characteristic and capacity with increasing current rates. The attenuated measured discharge curves of the cellular structure at 0.5C and 1C can be attributed due to the electrode thickness. Since only an electrode thickness of  $200 \mu\text{m}$  was used for the simulation compared to the experiment with a





**Figure 14.** Comparison of the simulation results of the discharge behavior for 0.5C, 1C, and 2C between the cellular and the lamellar structure. The gray dashed line symbolizes the discharge abort criteria of the measured cells.

sample thickness of 500  $\mu\text{m}$ , the results are consistent with the simulations in ref. [18], where the influence of different electrode thicknesses of a cellular structure was investigated. The thicker the electrode, the greater the damping effect on the voltage curve as SoC decreases. The cellular measurement exhibited a higher initial voltage drop and a smaller capacity during discharge. The simulation also showed the higher initial voltage drop for the cellular structure, which can be attributed to the poorer electrical conductivity due to the branching character of the cellular structure compared to the lamellar structure. At low currents or thin electrodes, the electrode structure plays a minor role, but it becomes more important with increasing thickness or current rates;<sup>[30,70]</sup> if the inhomogeneity is high and only a partial volume is selected, the uncertainty increases.

**Figure 14** shows a direct comparison of the simulation results of both electrode structures. The simulated capacities are quite similar for a 200  $\mu\text{m}$  thick electrode when the termination criterion is not limited to 2.5 V. The main differences are the aforementioned initial voltage drop and a slightly steeper gradient for the cellular structure. The simulation is not able to represent the reduced 0.5C ( $\approx 100 \text{ mAh g}^{-1}$ ) and 1C ( $\approx 40 \text{ mAh g}^{-1}$ ) capacity of the cellular structure. This result suggests that inhomogeneities within the cellular morphology have a much larger impact on the performance per electrode height than for the lamellar structure. Since it is not possible to simulate the entire electrode with a height of 500  $\mu\text{m}$  and a 10 mm diameter, due to both the limited field of view of the tomography and the limited computing power, compromises have to be made between reality and accurate simulation results. Our previous work has shown that good simulation results can be obtained by fitting the morphological parameters instead of using a clipped real 3D measured microstructure.<sup>[18]</sup>

### 3. Conclusion

In order to characterize the discharge behavior of freeze-casted LFP electrodes, an image-based numerical multiscale model for the investigation of real electrode structures at the microscale was successfully established. The microscale assumptions were sup-

ported by FIB/SEM analysis, which allowed a more precise parameterization down to the nanometer scale. The simulations confirmed that the physical model parameters, determined in previous work by a 2D parametric study approach, represent the lamellar structure quite well. The low current-dependent capacity simulation for the cellular structure was also in good agreement, but the uncertainty in the voltage profile and usable capacity increased with increasing C rates. The 3D model showed that for both electrode structures, the gradients of electrolyte concentration and SoL increased with C rate and depth of discharge in the direction of the electrode thickness up to a threshold of about 50  $\mu\text{m}$ , which can be attributed to the limitation of lithium-ion transport in the electrolyte. In addition, the uniformity of lithiation per height in the lamellar structure depended on the structure of each lamella itself, while the cellular structure showed a more uniform SoL per height due to its branching.

The approach to achieve higher model accuracy by using a clipped region of the real electrode structure instead of the estimated structural parameters of the whole electrode is limited by the clipped region and the computational power. However, parameter fitting can improve model accuracy, but the understanding of morphological dependencies remains elusive. In contrast, the tomographic approach visualizes the heterogeneities, makes it easier to understand the dependencies, and can identify bottlenecks between the lamellar and cellular electrode microstructure, which will help improve cell performance through optimized electrode structures. Despite the extensive morphological investigation, especially in the case of dynamic electrical measurements and aging scenarios, the nanostructures could lead to additional deviations between experiment and simulation, since these structures were only approximated here by the P2D approach with spherical particles.

This work demonstrates that electron transport through the electrode as well as ion transport through the porous electrode structure are key design parameters for electrodes thicker than 100  $\mu\text{m}$ , for example, linear electrolyte channels ensure a better lithium supply, minor branching in the current path reduces heat generation, and a continuous active material can be lithiated more homogeneously.

### 4. Experimental Section

**Fabrication of the  $\text{LiFePO}_4$  Electrodes and Swagelok Assembly:** The LFP/C slurry was prepared by adding  $\text{LiFePO}_4$  (LFP, Life Power P2 Phostech Lithium, Clariant) mixed with carbon black (CB, Super P Conductive, 99+%, Alfa Aesar) in a weight ratio of 95:5, an appropriate amount of a dispersant (DISPERBYK-190, Byk), and gelatin as a binder (from porcine skin, 170–195 g Bloom, medium gel strength for microbiology; Sigma-Aldrich) to deionized water. First, the deionized water was mixed with the gelatin and dispersing agent, and the LFP/C powder mixture was added. The suspension was then stirred with a magnetic stirrer for 30 min and finally deaerated under vacuum. The entire liquid solution was poured into a 10 mm diameter cylindrical mold and cooled from 25  $^{\circ}\text{C}$  ambient to  $-95^{\circ}\text{C}$  at a cooling rate of 2 K  $\text{min}^{-1}$  until the samples were completely solidified. In the final step, the water content of the sample was removed in a freeze dryer under  $\approx 0.08$  mbar vacuum at 20  $^{\circ}\text{C}$  for 24 h. The process parameters for the fabrication of the different structure types (lamellar and cellular samples) are shown in **Table 1**. The 20 mm high cylindrical samples were then sliced into 0.5 mm thin discs and dried overnight at 100  $^{\circ}\text{C}$  in an oven under argon gas. Both samples are expected to contain 87.2 wt%

**Table 1.** Processing parameters for the electrode fabrication distinguished into lamellar and cellular structure.

| Specimens | Liquid content [wt%] |     | Solid content [wt%] |         |                  | Process parameters                  |   |
|-----------|----------------------|-----|---------------------|---------|------------------|-------------------------------------|---|
|           | Dispersant           | LFP | CB                  | Gelatin | Temperature [°C] | Cooling rate [K min <sup>-1</sup> ] |   |
| Lamellar  | 67.3                 | 2.2 | 27.4                | 1.4     | 1.7              | 25                                  | 2 |
| Cellular  | 56.9                 | 2.8 | 36.1                | 1.9     | 2.3              | 25                                  | 2 |

**Table 2.** The governing equations of the COMSOL model. A detailed description of each equation can be found in Franke-Lang and Kowal (2021).<sup>[18]</sup>

| Region            | Equations                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |
|-------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| LFP electrode     | $\frac{\partial c_s}{\partial t} = \nabla \cdot (D_s \nabla c_s)$ $\varepsilon_l \frac{\partial c_l}{\partial t} = \nabla \cdot D_{l,eff} \nabla c_l - \frac{\nabla j_l \cdot t_+}{z \cdot F} + a_v \cdot j_{in} \cdot (1 - t_+)$ $j_s = -\sigma_{LFP,eff} \nabla \phi_s$ $-\nabla \cdot j_s = a_v \cdot j_{loc} = a_v \cdot z \cdot F \cdot j_{in}$ $j_{loc} = j_0 \left( \exp \left( \frac{\alpha_a F}{RT} \eta \right) - \exp \left( \frac{-\alpha_c F}{RT} \eta \right) \right)$ $j_0 = F \cdot (k_c)^{a_a} (k_a)^{a_c} (c_{s,max} - c_{s,k})^{a_a} (c_{s,k})^{a_c} \left( \frac{c_l}{c_{l,ref}} \right)^{a_a}$ $\eta = \phi_s - \phi_l - E_{eq}$ $j_l = \frac{2 \cdot \sigma_l RT}{z F^2} \left( 1 + \frac{\partial \ln(f_{\pm})}{\partial \ln(c_l)} \right) (1 - t_+) \nabla \ln(c_l) - \frac{\sigma_l}{z F} \nabla \phi_l$ |
| Electrolyte       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |
| Separator         | $\varepsilon_l \frac{\partial c_l}{\partial t} = \nabla \cdot D_{l,eff} \nabla c_l$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |
| Lithium electrode | $j_{loc,Li} = c_{ref,Li} \cdot F \cdot k_{Li} \left( \frac{c_l}{c_{ref,Li}} \right)^{a_{Li}} \left( \exp \left( \frac{(1 - \alpha_{Li}) \cdot F}{RT} \eta \right) - \exp \left( \frac{-\alpha_{Li} \cdot F}{RT} \eta \right) \right)$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |

LFP material after removal and drying of the liquid materials (i.e., water and ≈60 wt% dispersant). The sliced cathodes were finally prepared in an argon-filled glove box with lithium foil as the anode, a glass microfiber separator, and 1 M LiPF<sub>6</sub> in a 10:27:63 mixture of propylene carbonate (PC), ethylene carbonate (EC), and DMC as the electrolyte, and assembled in a Swagelok cell.

**Electrochemical Testing:** Discharge tests were performed with the assembled Swagelok cells in a climate chamber at room temperature using the Yokogawa GS610 potentiostat (Yokogawa Deutschland GmbH, Germany). The discharge cutoff voltage was set at 2.5 V. The cells were discharged at a constant C rate of C/2 and 1C, respectively. The specific capacity (capacity per unit weight of the active electrode material) was determined by integrating the applied current.

**Tomography Experiments and Image Data Processing:** All samples first have been measured at the BESSY II synchrotron facility (HZB, Berlin, Germany) using the BAMline beamline. A photon energy of 25 keV was used. For transmission image detection a combination of a CdWO<sub>4</sub> scintillator, a 10 times magnification optic and a PCO.4000 camera setup was used.<sup>[71]</sup> Each measurement consisted of 2200 projections over 180 degree. Additionally, 230 flatfields have been captured.

The FIB/SEM tomography was performed at the HZB CoreLab Correlative Microscopy and Spectroscopy (CCMS) using a ZEISS Crossbeam 350. For the serial section, the gallium gun was operated with an acceleration voltage of 30 keV and an ion current of 300 nA. Between each ion milling step, an SEM image was taken. For that the Gemini I electron gun was operated with an acceleration voltage of 2 keV, while the images have been detected with an angled chamber SE2 detector.

For the data analysis on the micrometer-scale, the synchrotron data was first reconstructed using the BAMline in-house filtered back projection-based algorithm.<sup>[72]</sup> For the FIB/SEM-data only a SIFT-based drift correction was needed.<sup>[73]</sup> For a precise analysis of the measured and reconstructed raw data however, a good classification was needed. First,

the synchrotron-based datasets were considered as a two-phase system (pore-active material). After denoising by means of a non-local means filter,<sup>[74]</sup> the application of an automated Otsu thresholding procedure was sufficient for the aimed binarization.<sup>[75]</sup> The final binary datasets have then been cropped and vectorized using paraview and meshlab.<sup>[76,77]</sup>

As shown in Figure 1c the FIB/SEM data had to be trinarized into the three phases: active material, carbon, and pores. Furthermore, adding to the complexity, the FIB/SEM measurement has been performed without embedding to allow for good carbon-phase detectability. The resulting difficult background reconstruction was performed by an HZB in-house U-Net-based neural network.<sup>[78]</sup> After background reconstruction and thus pore detection, an Otsu threshold was sufficient to distinguish between the two remaining classes (carbon and active material).

All the data processing and analysis have been performed using ImageJ,<sup>[79]</sup> Morpholib,<sup>[80]</sup> and OriginPro 2020. The two described complementary imaging techniques give a very different picture of the porosity and structure of the underlying materials due to their very different resolutions. While the synchrotron-based technique revealed a very different material structure, the FIB/SEM tomography showed that the underlying nanostructure, the building block so to say, consists of identical isotropic porosity behavior in both samples.

**3D Electrochemical Model:** The 3D model of the half cell was based on the P2D approach of Doyle et al.<sup>[34]</sup> and Newman and Tiedemann<sup>[81]</sup> and the equations were solved numerically using the commercial software COMSOL Multiphysics V5.5. The equations used have already been presented in a preliminary theoretical study.<sup>[18]</sup> The mass transport within the electrolyte was fundamentally described by the Nernst-Planck equation, while the lithium transport in the electrode was implemented by the second Fick's Law. The charge transfer was modeled by a Butler-Volmer dependence. The governing equations depending on the model region are shown in Table 2. The additional electrochemical and design parameters are listed in Table 3.

**Table 3.** Electrochemical and design parameters applied in the model.

| Parameter           | Description                       | Lamellar electrode    | Cellular electrode    | Separator             | Current collector | Unit                |
|---------------------|-----------------------------------|-----------------------|-----------------------|-----------------------|-------------------|---------------------|
| $w_i$               | Width                             | 200                   | 200                   | 200                   | 200               | $\mu\text{m}$       |
| $h_i$               | Thickness                         | 200                   | 200                   | 45                    | 50                | $\mu\text{m}$       |
| $r_p$               | Particle radius                   | 120                   | 120                   | —                     | —                 | nm                  |
| $\epsilon_s$        | LFP filler fraction               | 0.464                 | 0.459                 | 0.276                 | 1                 | —                   |
| $\epsilon_i$        | Electrolyte filler fraction       | 0.518                 | 0.523                 | 0.724                 | 0                 | —                   |
| $c_{s,\text{max}}$  | Total solid-phase concentration   | 16 481                | 16 481                | —                     | —                 | $\text{mol m}^{-3}$ |
| $c_{i,\text{init}}$ | Initial electrolyte concentration | 1000                  | 1000                  | 1000                  | —                 | $\text{mol m}^{-3}$ |
| $c_{s,\text{init}}$ | Initial solid-phase concentration | 16.481                | 16.481                | —                     | —                 | $\text{mol m}^{-3}$ |
| $\sigma_i$          | Electrical conductivity           | 2                     | 2                     | 0.053                 | $3.7 \times 10^7$ | $\text{S m}^{-1}$   |
| $D_i$               | Diffusion coefficient             | $4.5 \times 10^{-19}$ | $4.5 \times 10^{-19}$ | $1.3 \times 10^{-10}$ | —                 | —                   |
| $\tau_i$            | Tortuosity                        | 1.04                  | 1.04                  | 1.08                  | —                 | —                   |

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Keywords

electrochemical model, electrode optimization, focused ion beam scanning electron microscopy, freeze casting,  $\text{LiFePO}_4$ , Li-ion batteries, X-ray tomography

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